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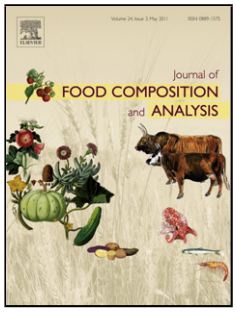

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Original Research Article

Determination of cadmium and lead in wine samples by means of dispersive liquid-liquid microextraction coupled to electrothermal atomic absorption spectrometry

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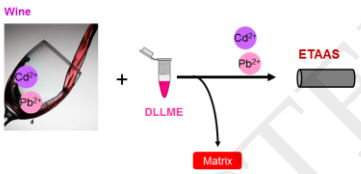
Graphical abstract



Highlights

- DLLME is successfully employed for Cd and Pb analysis in wine samples by ETAAS
- DLLME affords lower LoDs than the previously reported wine analysis methodologies
- Lead determination is free from both spectral and non-spectral interferences
- Cadmium determination is strongly affected by the presence of Zn in wine

Abstract

Wine contains significant amounts of Cd and Pb coming from different contamination sources. The analysis of these elements still means an enormous challenge due to its low concentration levels and the complexity of the wine matrix. Therefore, new highly sensitive analytical methods are currently required. The present work reports a new method based on the use of dispersive liquid-liquid microextraction (DLLME) and electrothermal atomic absorption spectrometry (ETAAS) determination. Results demonstrate that, under optimum DLLME experimental conditions, accurate Pb determination can be easily performed using external calibration. Cadmium determination requires a standard addition calibration strategy since its accuracy is strongly affected by the presence of Zn in the wine matrix. The limits of detection afforded by the method proposed were 0.01 and 0.08 μg L^{-1} for Cd and Pb, respectively. These values were around one order of magnitude lower than those previously reported for wine analysis by ETAAS. This simple methodology has been successfully employed for Cd and Pb analysis in different types of wines (i.e., white, red, rosé and sparkling wines). The results are in agreement with those obtained by Inductively Coupled Plasma – Mass Spectrometry after a time-consuming microwave-assisted acid digestion treatment.

Keywords:, food analysis, food composition, wine, cadmium, lead, sample preparation, dispersive liquid-liquid microextraction, electrothermal atomic absorption spectrometry

1. Introduction

Wine is one of the most widely consumed beverage around the world. Nevertheless, it exhibits significant Pb and Cd levels (i.e. low-medium μg L^{-1} range) that are mainly related to atmospheric contamination, pesticides and materials used in wine production, transport and storage (Pyrzynska, 2004; Pohl, 2007). Due to their hazardous nature, Cd and Pb maximum allowed levels in wine are regulated worldwide (EC, 2006; OIV, 2016). Thus, for instance, the Organisation Internationale de la Vigne et du Vin (OIV) limits Cd and Pb in wine to 10 μg L^{-1} and 150 μg L^{-1}, respectively (OIV, 2016).

Cadmium and Pb analysis in wine is usually carried out by means of spectrometric techniques (Grindlay et al., 2011). Among them, mainly when no multi-element analysis is required, electrothermal atomic absorption spectrometry (ETAAS) is the most preferred choice due to its high selectivity and low limits of detection (LODs). Direct wine analysis by ETAAS is difficult due to the occurrence of both spectral and non-spectral interferences originated from wine matrix components (organics and salts) (Grindlay et al., 2011). For instance, non-volatile organic components of wine are a source of non-specific background absorption and affect long-term reproducibility because of the accumulation of carbonaceous residues after several graphite tube firings (Freschi et al., 2001; Ajtony et al., 2008). To deal with these interferences, some strategies can be applied: (i) a judicious optimization of ETAAS temperature program and modifier selection (Freschi et al., 2001; Kristl et al., 2002; Karadjova et al., 2004; Dessuy et al., 2008; Ajtony et al., 2008); (ii) the

use of transversally heated furnaces (Freschi et al., 2001; Dessuy et al., 2008); (iii) a Zeeman-based background correction (Freschi et al., 2001; Kim, 2004; Ajtony et al., 2008); and/or, (iv) the use of a sample pre-treatment step prior to the analysis. To this end, acid digestion (Kim, 2004; Capelo et al., 2005; Ajtony et al., 2008) or dilution (Freschi et al., 2001; Karadjova et al., 2007) have been employed but at the expense of the sample throughput and detection capabilities. Solid-phase extraction/preconcentration procedures using different type of columns have been also reported for the quantification of Cd and Pb in wines by flame atomic absorption spectrometry (FAAS) (Lemos et al., 2002; Bakircioglu et al., 2003; Tuzen & Soylak, 2004; Tuzen et al., 2005) at the concentration levels imposed by regulatory authorities. Up to date, the use of extraction/preconcentration procedures for Cd and Pb analysis in wine by means of ETAAS have not been investigated in detail though its potential advantages to reduce both spectral and non-spectral interferences derived from wine matrix.

Dispersive liquid-liquid micro-extraction (DLLME) has been stablished as a faster and greener sample preparation methodology than conventional liquid-liquid extraction and solid phase extraction approaches for elemental analysis (Zgoła-Grzeskowiak & Grzeskowiak, 2010; El-Shahawi & Al-Saidi, 2013). DLLME improves LODs and sample throughput as well as minimizes matrix effects, reagents requirements and waste generation. Different spectroscopic techniques have been employed to analyze DLLME extracts (Kocot et al., 2016). Nevertheless, ETAAS is usually preferred due to its good capability to deal with micro-volume samples and organic solvents (Andruch et al., 2013; de

la Calle et al., 2016). DLLME has been traditionally employed for metal analysis in water samples and, in a lesser extent, in foods (Andruch et al., 2013). Very little research has been performed evaluating the potential benefits (and drawbacks) of DLLME for inorganic analysis in wine samples. Seeger et al. (2015) employed DLLME for Cu and Fe determination in wine by FAAS. Results afforded by DLLME-FAAS were comparable to those obtained by means inductively coupled plasma atomic emission spectrometry (ICP-AES) after an acid digestion treatment. However, sample throughput was partially compromised due to the mandatory use of standard addition calibration strategy due to the high matrix effects originated by the organic extracts in the flame. Escudero et al. (2013), successfully employed a DLLME procedure for As speciation in wine by ETAAS. Experimental results show that As^{3+} extraction was highly selective and free from interferences originated by inorganic concomitants present in wine. To our best knowledge, no further works related on this topic have been reported.

The goal of this work is to develop a new analytical method for Cd and Pb determination in wine by means of DLLME-ETAAS. To this end, both DLLME (i.e. extractant mass, disperser type and volume, pH and ionic strength) and ETAAS (i.e. modifier and temperature program) experimental parameters have been optimized. Finally, the developed methodology has been applied to the analysis of different wine samples (white, rosé, red, sparkling and fortified). To evaluate the results obtained, wine samples have also been analyzed by means of inductively coupled plasma - mass spectrometry (ICP-MS) after a digestion procedure.

2. Experimental

2.1 Reagents

1-butyl-3-methyl-imidazolium hexafluorophosphate ($BmimPF_6$, ≥97%, sodium diethyldithiocarbamate trihydrate (DDTC, ≥99%), methanol (≥99.9%), ethanol (≥99.5%), sodium chloride (≥99.5%) and Pb, Cd and Pd mono-elemental standard solutions (1000 mg L^{-1}) were obtained from Sigma-Aldrich (Steinheim, Germany). Nitric acid (69% w w^{-1}), sodium dihydrogen phosphate (≥99.5%), disodium dihydrogen phosphate (≥99.5%), glacial acetic acid (99.7%), sodium acetate (99%) and potassium nitrate (99%) were purchased from Merck (Darmstadt, Germany). Calcium nitrate hexahydrated (99%), copper nitrate trihydrate (99%), iron (III) nitrate (98%), manganese nitrate (≥98.5%), magnesium nitrate (99%), strontium nitrate (99%) and zinc nitrate hexahydrate (98.5%) were obtained from Scharlab (Barcelona, Spain).

All solutions were prepared using high purity water (i.e. with conductivity lower than 18 MΩ cm-1) obtained from a Milli-Q water system (Millipore Inc. Paris, France).

2.2 Wine samples

Five Spanish wine samples, purchased in local markets, were analysed to cover different matrix characteristics and ethanol content: white (Fidencio, Spain, 11.5% w w^{-1}), rosé (Piccolo Giovanni, Italy, 9.0% w w^{-1}), sparkling (Cava Jaume Serra, Spain, 11.5% w w^{-1}), fortified (Mistela Murviedro, Spain, 15% w w^{-1}) and red wine (Fidencio crianza, Spain, 13.5% w w^{-1})

2.3 Dispersive liquid-liquid microextraction

The extraction/preconcentration procedure for Cd and Pb determination was performed as follows. First, 2 mL of wine sample or analyte standard were placed on a centrifuge tube with 100 µL of the suitable buffer solution (e.g. acetic acid/sodium acetate dyhidrogen/hydrogen phosphate). Then, 100 µL of NaCl and 100 µL of the DDTC solutions were added. Next, a mixture of $BmimPF_6$ (extractant) and methanol (disperser) was injected using a 1.00 mL syringe and the resulting system was shaken for 2 minutes using a vortex. To separate the two phases generated (water/ionic liquid), the mixture was centrifuged for 5 minutes at 3500 rpm. The lower layer of the ionic liquid was removed with a micropipete and then diluted with methanol ($BmimPF_6$/methanol 1:1 ratio) prior to ETAAS analysis.

2.4 Microwave digestion

For comparison, wine samples were analyzed by ICP-MS (model 7700x, Agilent, Santa Clara, USA) after a microwave assisted digestion treatment in closed vessel. To this end, 5 g of the selected wine was weighed into a PTFA digestion vessel and 5 mL of concentrated nitric acid was added. The mixture was allowed to react and after clearance of fumes (20 min) the vessel was closed. Afterwards, samples were digested in a Star D microwave digestion system (Milestone, Shelton, CT, USA) using the program recommended by the manufacturer. Finally, the digested samples were made up to 20 g with water.

2.5 Instrumentation

Cadmium and Pb in DLLME extracts were determined using an atomic absorption spectrometer (model 2100, Perkin Elmer, Norwalk, USA) equipped with a graphite furnace atomizer and a deuterium background correction system. Samples were introduced into the furnace by an auto-sampler (model AS-60, Perkin Elmer, Norwalk, USA). Pyrolytically coated graphite tubes without platform were used in this work. Cadmium and Pb signals were measured using the optimized temperature programme given in Table 1. For comparison, wine samples were also analyzed by ICP-MS. Instrumental and experimental conditions employed in ICP-MS are described elsewhere (Abdrabo et al., 2015).

3. Results

3.1. Optimization of graphite furnace experimental conditions

Ionic liquids are considered safer and more environmentally friendly than the (volatile) organic solvent traditionally employed in DLLME procedures. In the present work, $BmimPF_6$ has been selected as extraction media. However, direct analysis of Cd and Pb in $BmimPF_6$ extracts by ETAAS is not straightforward due to the physical properties of both ionic liquid (low volatility and high viscosity) and analytes (high volatility). First, the high viscosity of $BmimPF_6$ (i.e. 381 cP at 25°C) makes difficult the sample handling. The direct introduction of ionic liquids into the furnace by means of a syringe (Manzoori et al., 2009; Lopéz-García et al., 2013) did not afford reproducible results for Pb and Cd analysis even when using an autosampler. To solve this drawback, Li et al. (2009) proposed to reduce the $BmimPF_6$ viscosity by dilution with an

appropriate solvent (e.g. alcohols). In the present work, it was observed that irrespective of the dilution factor used (ranging from 1:0.5 to 1:3), $BmimPF_6$:methanol mixtures were easily introduced in the furnace by the autosampler with high reproducibility. Therefore, to reduce the analyte dilution, a 1:0.5 $BmimPF_6$:methanol dilution ratio was first selected after the DLLME procedure. Nonetheless, high background signals were registered irrespective of the modifier and temperature program employed and even using a deuterium correction system. Better results were obtained by employing a 1:1 $BmimPF_6$:methanol mixture.

3.1.1. Modifier

In this work, palladium (as a nitrate salt) was selected as matrix modifier since it is usually employed for the analysis of Cd and Pb in carbon containing matrices (Freschi et al, 2001; Kristl et al., 2002; Dessuy et al., 2008; Ajtony et al. 2008; Grindlay et al., 2009; López-García et al., 2013) avoiding the structured background caused by other modifiers (i.e. phosphates) (Welz, 1999; Kristl et al., 2002; Ajtony et al., 2008). To check the influence of the palladium concentration on the absorbance of Cd and Pb, standard solutions of these elements (with a final concentration of 1 and 10 μg L^{-1}, respectively) with amounts of Pd ranging from 0.5 to 9 μg were prepared in a 1:1 $BmimPF_6$:methanol mixture. Experimental results shown that the use of Pd makes feasible to use higher pyrolysis temperatures thus reducing the background signal. Cadmium and Pb absorbance increased with Pd concentration up to 1 μg of Pd. For higher Pd concentrations, no noticeable

effect was observed on the absorbance of both elements. Therefore, the amount of modifier was kept at 1 µg for further experiments.

3.1.2. Furnace temperature program

Taking into account the high temperatures required to decompose $BmimPF_6$ (>350ºC), a two-step pyrolysis procedure was selected to reduce background signals (Li et al., 2009; Berton & Wuilloud, 2010; Stanisz & Zgoła-Grześkowiak, 2013). The pyrolysis temperature was initially set at 350º C for 20 seconds and, then, it was increased up to values ranging from 400 to 1200ºC for 20 extra seconds. Fig. 1 shows the pyrolysis and atomization curves for Cd and Pb. In this figure, absorbance of both elements were normalized against their respective maximum value. As it can be observed in Fig. 1.A, absorbance remains constant up to pyrolysis temperatures of 800-900ºC. Nevertheless, it is interesting to note that, when increasing the pyrolysis temperature from 400ºC up to the above-mentioned values, background signal was reduced approximately 3-fold. Due to these reasons, pyrolysis temperatures of 800ºC and 900ºC were selected for Cd and Pb, respectively. With regard the atomization temperature (Fig 1.B), the optimum value obtained for both elements was of 1600ºC. These temperatures are similar to those reported by other authors operating with different ionic liquids (i.e., 1-octyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (López-García et al., 2013) and 1-hexyl-3-methylimizadolium hexafluorophosphate (Li et al., 2009). Finally, it is worth to mention that no significant memory effects were observed due to carbon deposition in the furnace after several graphite firings, thus ensuring the

reproducibility of the signal measurements (5-10%).

3.2. Optimization of DLLME experimental conditions

Optimization of the DLLME procedure was carried out using 2 mL of a synthetic wine sample containing 12.5% v v^{-1} ethanol and potassium 1000 mg L^{-1} (i.e. the major organic and inorganic wine components). The variables tested were: (i) DDTC concentration (chelating agent); (iii) pH; (iii) ionic strength; (iv) $BmimPF_6$ mass (extractant solvent); and (v) methanol volume (disperser solvent).

3.2.1 Effect of chelating agent concentration and pH

Metal extraction into the ionic liquid relies on the formation of a neutral chelate with DDTC. Fig. 2 shows the influence of DDTC concentration on the absorbance of Cd and Pb. As it can be observed, absorbance for both elements increased with DDTC concentration up to 1.0 %. Above this value, no significant signal improvement was observed.

Solution pH also plays a significant role on the metal-chelate formation and, hence, on the Cd and Pb extraction. The influence of the pH on analyte extraction was investigated in the pH range from 3 to 9 (Fig. 3). No significant influence of the solution pH on Cd absorbance was observed. Nevertheless, Pb signal shows a maximum at pH values around 6-7. From these findings, DDTC concentration and pH were set at 1% v v^{-1} and 6, respectively.

3.2.2. Effect of solution ionic strength

The influence of the ionic strength on Cd and Pb extraction from the aqueous

phase to the organic phase was investigated using synthetic wine samples spiked with variable amounts of NaCl (0-15% w v^{-1}). Cadmium and Pb absorbance showed a maximum for the solution containing 5.0 % w v^{-1} NaCl. These results suggest that analyte extraction is partially favoured by increasing the media ionic strength. Therefore, this optimum NaCl concentration was employed in further experiments.

3.2.3 Effect of the amount of extractant

To evaluate the influence of $BmimPF_6$ amount on Cd and Pb extraction, ionic liquid masses ranging from 150 to 300 mg were tested. $BmimPF_6$ masses lower than 150 mg were not explored due to the lack of reproducibility in drop formation and the low masses of ionic liquid recovered after the DLLME treatment (<15 µg). It was observed that Cd and Pb absorbance decreased when increasing the amount of $BmimPF_6$. These findings are easily explained taking into account that analyte preconcentration factor is reduced when increasing the mass of extractant (Li et al., 2009; Yousefi & Shemairini, 2010; Khan et al., 2013). Therefore, a $BmimPF_6$ mass of 150 mg was selected for further studies.

3.2.4. Effect of the disperser solvent nature and volume

Two organic solvents (methanol and acetone) were tested as potential dispersers for $BmimPF_6$. Results shown that Cd and Pb signals were on average 1.2-fold higher for methanol than for acetone. Similar findings were obtained by Khan et al. (2013) operating $BmimPF_6$ for Cd extraction with 1-(2-

pyridylazo)-2-naphthol in environmental and biological samples. Fig. 4 shows the influence of methanol volume on the normalized Cd and Pb absorbance in ETAAS. As it can be observed, absorbance for these elements increases with methanol volume up to 600 µL due to a higher extraction efficiency of the metal-chelate complex from the water to the organic phase. Volumes higher than 600 µL were not employed due to the lack of $BmimPF_6$ droplet formation after the DLLME treatment. These results suggest that the $BmimPF_6$ solubility in the synthetic wine standards is favored by the disperser solvent. In fact, this issue was not found operating ethanol-free wine standards. Therefore, methanol volume was set at 600 µL.

3.3. Analytical figures of merit

Due to the lack of a certified wine reference material for Cd and Pb analysis, method accuracy was evaluated by means of a recovery test using different wine samples. Taking into account the levels usually found for these elements in wines, samples were spiked with 1 µg L^{-1} of Cd and 10 µg L^{-1} of Pb. The assay was performed using the optimum ETAAS and DLLME operating conditions described in the previous sections. Results for the recovery test are reported in Table 2. As it can be observed, Pb recovery was almost quantitative (96-100%), regardless the wine sample selected. However, results obtained for Cd were systematically lower (i.e., 20-79% lower) than the expected ones. These results suggest that other elements present in wine are affecting the Cd extraction. According to the literature (Grindlay et al., 2011), along with potassium, wines contain significant amounts of: (i) Ca (100 mg L^{-1}); (ii) Mg

(100 mg L^{-1}); (iii) Fe (4 mg L^{-1}); (iv) Cu (1 mg L^{-1}); and (v) Zn (1 mg L^{-1}). Thus, to insight on the origin of the poor Cd recoveries obtained, different synthetic wine (12% v v^{-1} ethanol and 1000 mg L^{-1} potassium) matrices containing each of the above-mentioned concomitants were prepared. Cadmium recovery was quantitative for all the matrices tested except for the Zn containing one. Thus, when operating matrices containing Zn levels below 0.5 mg L^{-1}, Cd recoveries were quantitative. From this concentration on, Cd recoveries always decrease when increasing the concentration of Zn present in the matrix. At concentrations of 1 mg Zn L^{-1}, Cd recovery was found of 76±4%. Taking into account these findings, Zn concentration was determined in all the wine samples tested. As expected, a direct correlation between Zn levels and Cd recovery was found (Table 2). Sothe highest Cd recoveries were obtained for those samples containing the lowest Zn concentration levels.

As regards the precision of Cd and Pb measurements, the relative standard deviation obtained after the analysis of five independent replicates range between 4-9% (values typically obtained in ETAAS).

Cadmium and Pb LODs were calculated using the calibration graph according to the method described by Hubuax et al. (i.e. based on 5 standards, 95% confidence level) (Hubaux & Vos, 1970). LODs obtained for Cd and Pb were 0.01 and 0.08 µg L^{-1}, respectively. As reported in Table 3, these values were about 8 and 9-fold lower than those obtained in ETAAS using a direct analysis method (i.e., without DLLME). These improvement factors are in agreement with the experimental enrichment factors obtained for Cd and Pb when operating with DLLME. These results suggest that LODs could be further

improved by increasing the analyte enrichment factor. In fact, LoDs obtained in this work are higher than those reported in the literature using other DLLME procedures for Cd and Pb analysis by ETAAS(de la Calle et al., 2016). It can be explained taking into account that in the method proposed, the extraction with $BmimPF_6$: (i) requires a dilution with methanol prior to the sample introduction into the graphite furnace, thus reducing the analyte enrichment factor. In addition, also the sample volume used in this work was at least between 2.5 and 5-fold lower than those usually reported due to the limited volume of the centrifuge tubes employed; and, (ii) is negatively affected by the presence of ethanol in the wine matrix. In spite of these facts, data in Table 3 clearly demonstrate that the LODs obtained with the method proposed in this work are lower than those previously reported for Cd and Pb in wines by ETAAS using alternative sample preparation methodologies. In addition, the proposed method reduces both instrumental analysis complexity and costs since it does not require neither time consuming digestion treatments nor complex background correction systems to deal with spectral interferences.

3.4. Analysis of wine samples

Five wine samples have been analyzed to quantify Cd and Pb levels using the methodology developed. Lead analysis was performed by means of calibration with standards containing ethanol 12% v v^{-1} and 1000 mg K L^{-1}. Given the variability of the Zn content in the wine samples, standard addition was chosen as the calibration strategy for Cd analysis. Other approaches (e.g. Zn matched standards, additional extraction treatments) were not investigated due to their

higher complexity as well as their negative impact on the benefits derived of using DLLME for sample preparation (e.g. sample throughput, simplicity, etc.). Results obtained were compared to those obtained using a microwave acid sample digestion procedure and ICP-MS detection. Wine digestion decompose organic components mitigating carbon matrix effects. As it can be derived from data shown in Table 4, no significant difference was found in the Pb concentration values obtained by DLLME-ETAAS and ICP-MS. Lead concentration levels in the tested wine samples agreed with those previously reported (Grindlay et al., 2009). Cadmium concentration levels in all the samples tested were below the LoD of both DLLME-ETAAS and ICP-MS (Table 4).

4. Conclusions

Results reported in this work demonstrate that DLLME using ionic liquids is a very simple and useful sample-pre-treatment methodology for accurate determination of Cd and Pb in wine samples by ETAAS. Cadmium extraction in $BmimPF_6$ is strongly affected by the presence of Zn in wine samples. As a consequence, the use of a standard addition calibration strategy is mandatory for this element. Under optimum conditions, the LoDs obtained for Cd and Pb are lower than those previously reported in ETAAS using conventional sample preparation strategies (i.e., sample dilution, digestion and direct analysis). These results highlight the great potential of DLLME for metal analysis in wine but further research is still required mainly to improve the method selectivity (especially for Cd) and LoDs.

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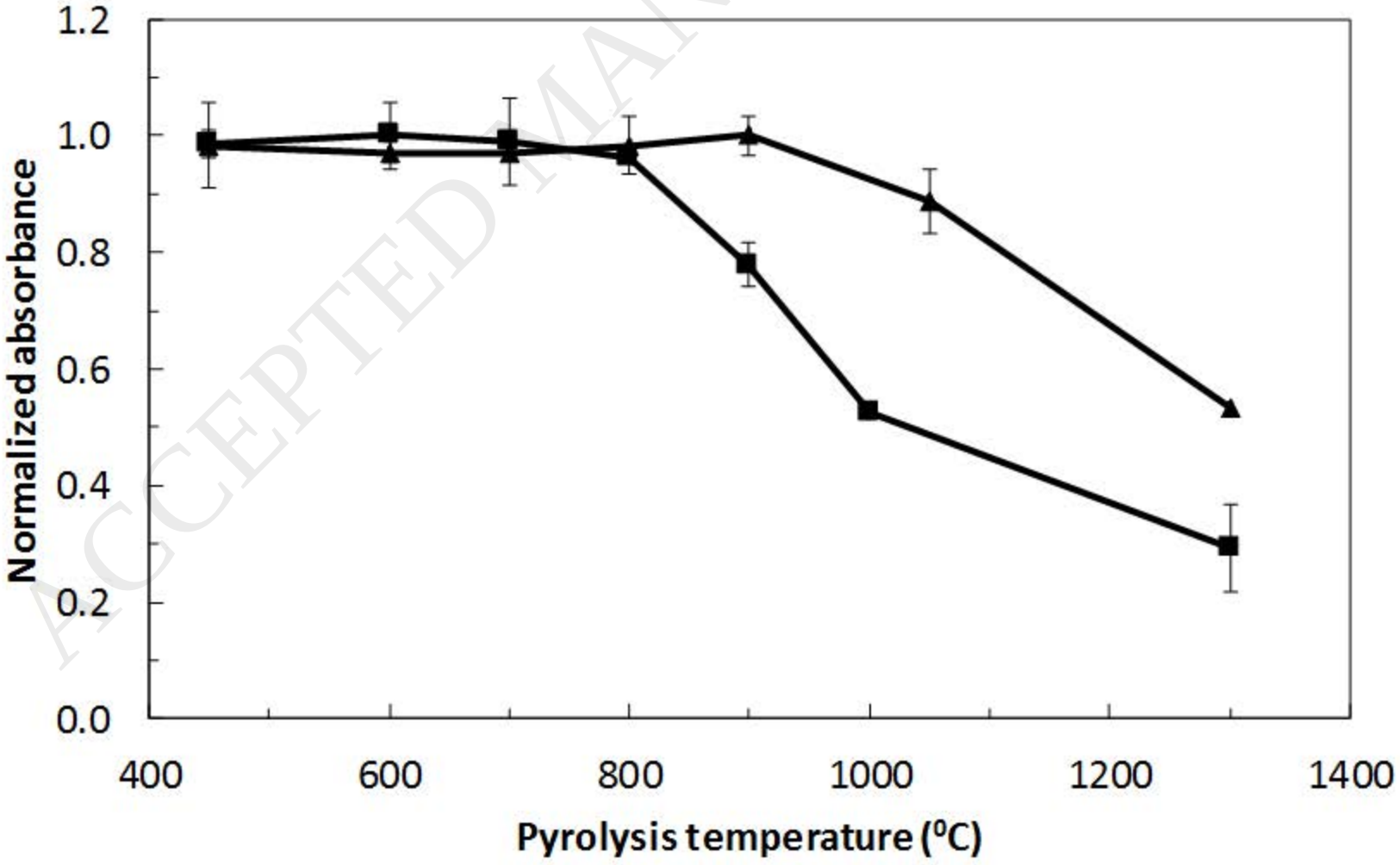
Figure captions

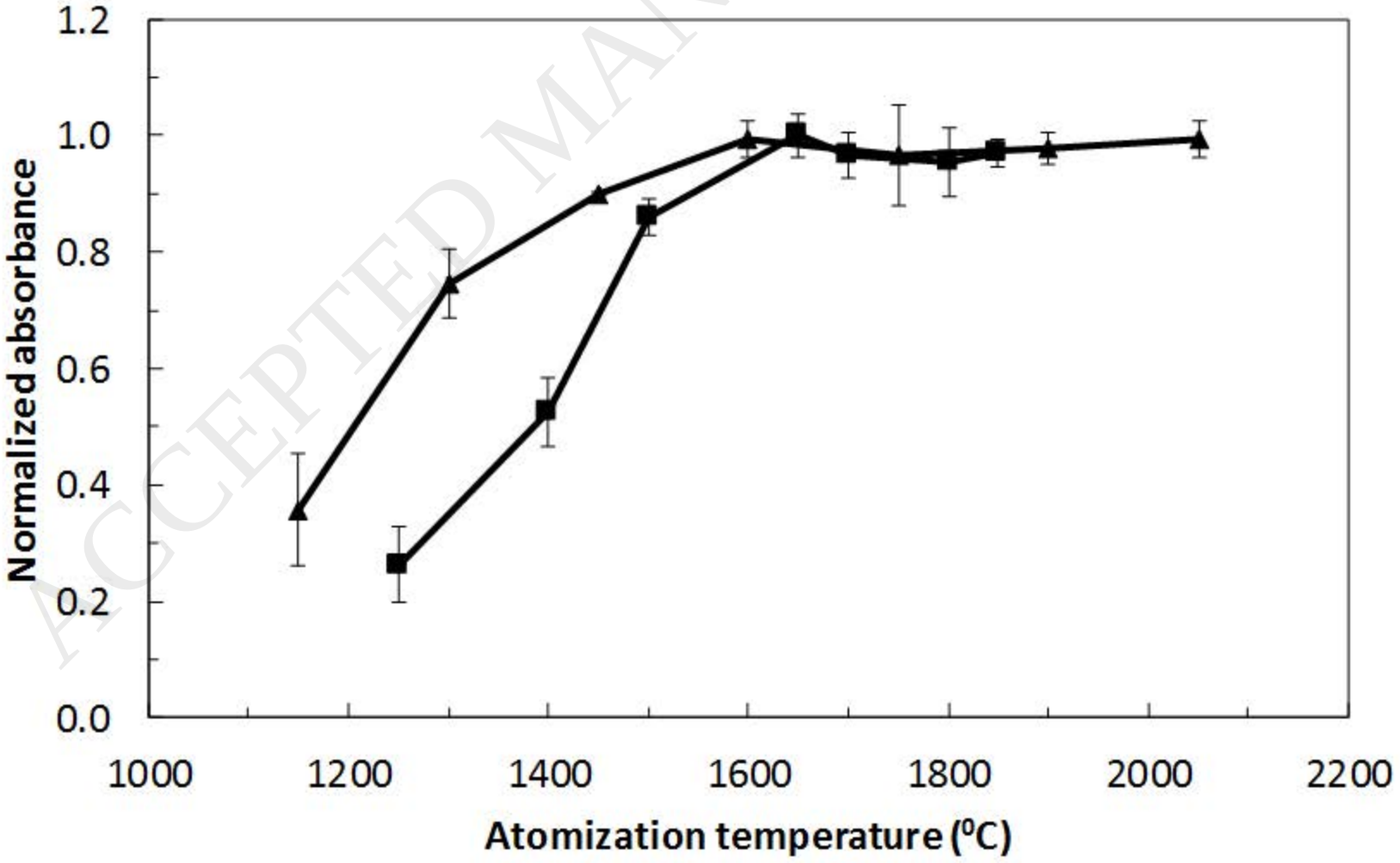
Fig. 1. Influence of the pyrolysis (A) and atomization (B) temperature on the normalized absorbance for Cd (**-■-**) and Pb (**-▲-**) in ETAAS. Modifier:1 µg Pd. Atomization temperature in (A): Cd and Pb: 1600ºC; Pyrolysis temperature in (B): Cd 800ºC, Pb 900ºC.

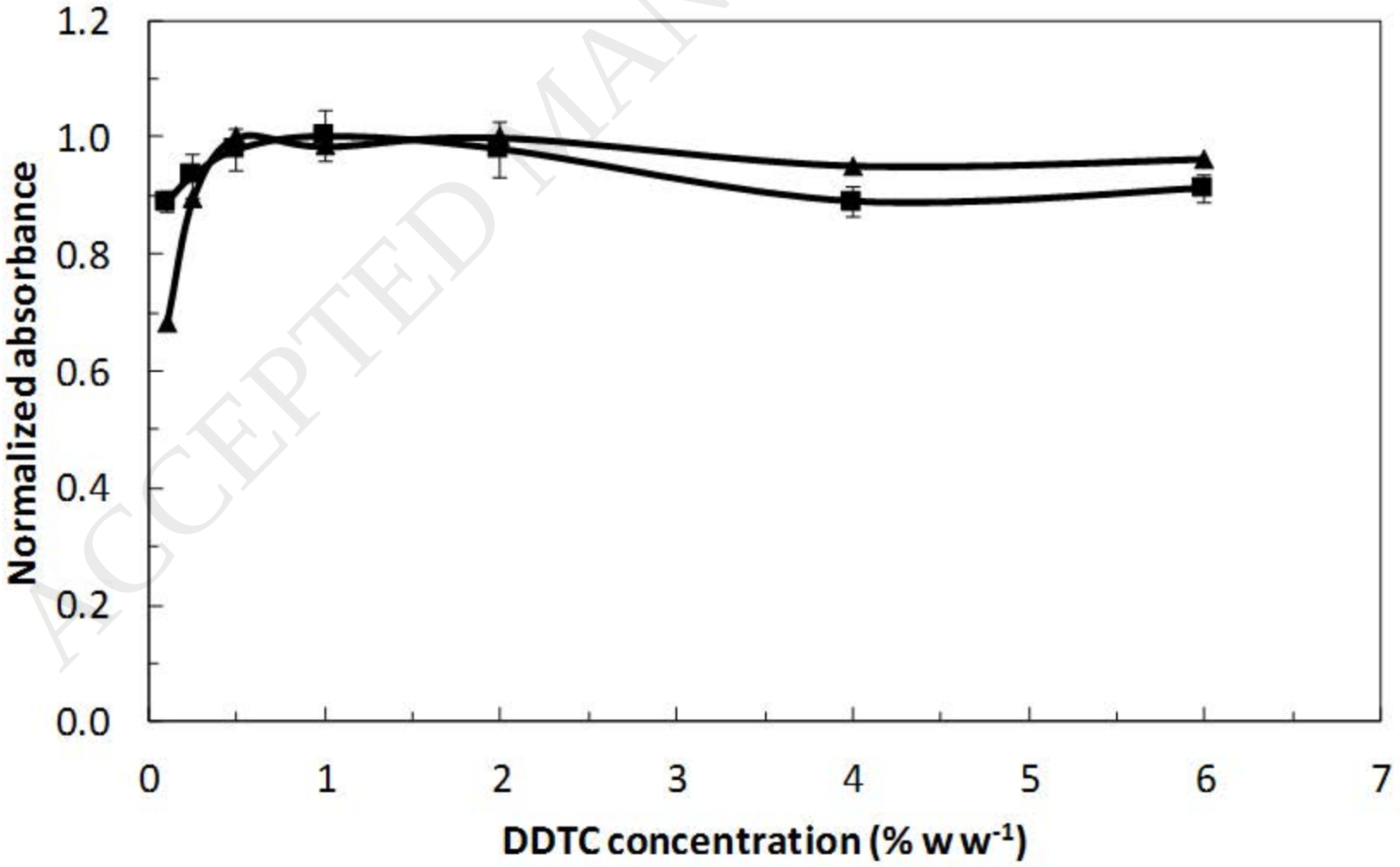
Fig. 2. Influence of the DDTC on the normalized absorbance for Cd (**-■-**) and Pb (**-▲-**) in ETAAS. $BmimPF_6$ mass: 150 µg; Methanol volume: 600 µL; solution pH: 6; NaCl concentration: 5.0% w w^{-1}.

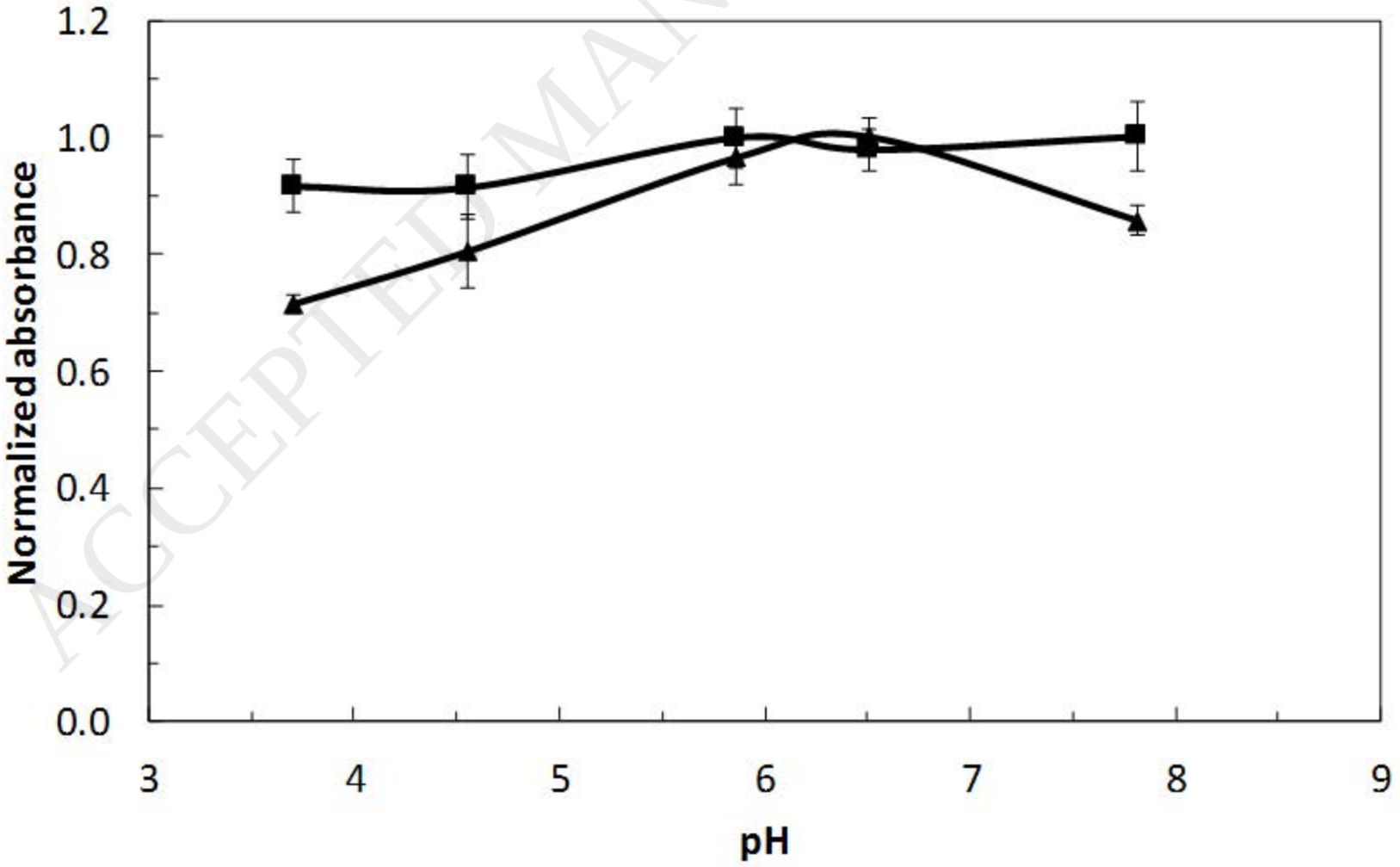
Fig. 3. Influence of the solution pH on the normalized absorbance for Cd (**-■-**) and Pb (**-▲-**) in ETAAS. $BmimPF_6$ mass: 150 µg; Methanol volume: 600 µL; DDTC concentration: 1.0 w w^{-1}; NaCl concentration: 5.0% w w^{-1}.

Fig. 4. Influence of the disperser volume on the normalized absorbance for Cd (**-■-**) and Pb (**-▲-**) in ETAAS. $BmimPF_6$ mass: 150 µg; DDTC concentration: 1.0 w w^{-1}; solution pH: 6; NaCl concentration: 5.0% w w^{-1}.









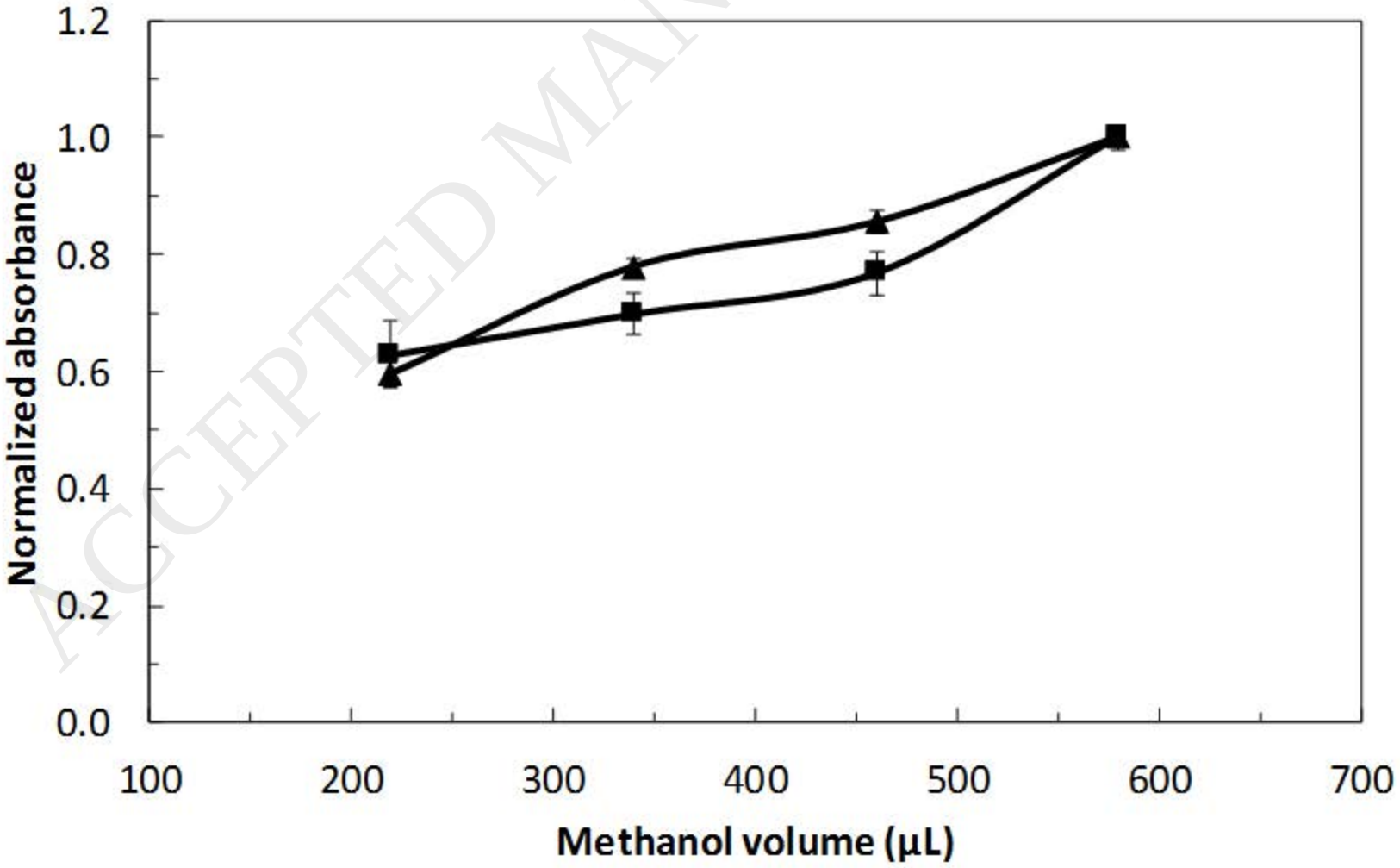


Table 1. ETAAS operating conditions

Parameter		**Lead**	**Cadmium**
Lamp current (mA)		9	8
Wavelenght (nm)		283.3	228.8
Spectral bandwith (nm)		0.7	
Injected volume (µL)		20	
Furnace heating program			
Step	**Temperature (ºC)**	**Ramp (s)**	**Hold (s)**
Dry	100	20	10
Pyrolysis	350	10	20
	400-1300	10	20
Atomization	1000-2100	1.0	5
Clean	2600	1.0	3

Table 2. Recovery values for Cd and Pb by DLLME-ETAAS and concentration of Zn present in the different wine samples.

Type of wine	Recovery (%)*		Zn (μg L^{-1})*
	Pb	Cd	
White	98±4	79±5	800±30
Rosé	99±5	52±4	1400±90
Sparkling	98±4	51±6	1300±100
Fortified	100±3	36±4	2100±180
Red	96±4	20±5	2800±130

*Mean ± standard deviation, 5 replicates

Table 3. Comparison of the LOD obtained using the diverse methodologies reported for Cd and Pb determination in wine by electrothermal-based spectroscopic techniques.

Element	Sample preparation	Background correction	LOD (μg L^{-1})	Reference
Cd	Direct analysis	Deuterium	0.08	This work
	DLLME	Deuterium	0.01	
	Direct analysis	Zeeman	0.03	Ajtony et al., 2008
	Digestion	Zeeman	0.1	Kim, 2004
	Dilution	Zeeman	0.03	Freschi et al., 2001
Pb	Direct analysis	Deuterium	0.16	This work
	DLLME	Deuterium	0.08	
	Direct analysis	Zeeman	0.8	Ajtony et al., 2008
	Digestion	Zeeman	1.0	Kim, 2004
	Dilution	Zeeman	0.8	Freschi et al., 2001

Table 4. Lead and cadmium concentration values in the different wine samples by means of DLLME-ETAAS and ICP-MS.

Type of wine	Pb (μg L^{-1})*		Cd (μg L^{-1})*	
	DLLME-ETAAS	ICP-MS	DLLME-ETAAS	ICP-MS
White	2.0±0.2	1.8±0.1	< 0.01	
Rosé	2.17±0.16	2.14±0.07	< 0.01	
Sparkling	1.75±0.15	2.0±0.1	< 0.01	
Fortified	1.8±0.3	1.7±0.1	< 0.01	
Red	2.7±0.2	2.7±0.2	< 0.01	

*Mean ± standard deviation, 5 replicates